Toxicology Reports 5 (2018) 654–670

Contents lists available at ScienceDirect

Toxicology Reports

journal homepage: www.elsevier.com/locate/toxrep

Assessment of metal levels in foodstuffs from the Region of Valencia (Spain)

Silvia Marín[a], Olga Pardo[a,b], Alfredo Sánchez[a], Yovana Sanchis[a], Dinoraz Vélez[c], Vicenta Devesa[c], Guillermina Font[d], Vicent Yusà[a,b,*]

[a] Food Safety Research Area, Foundation for the Promotion of Health and Biomedical Research of Valencia Region, FISABIO. Av. Catalunya, 21, 46020, Valencia, Spain
[b] Analytical Chemistry Department. University of Valencia, Av. Vicent Andrés Estellés s/n, 46100 Burjassot, Valencia, Spain
[c] Institute of Agrochemical and Food Technology (IATA-CSIC). Av. Agustín Escardino no 7, 46980 Paterna, Valencia, Spain
[d] Preventive Medicine and Public Health, Food Sciences, Toxicology and Forensic Medicine Department, University of Valencia, Av. Vicent Andrés Estellés s/n, 46100 Burjassot, Valencia, Spain

ARTICLE INFO

Keywords:
Metals
Foodstuffs
Occurrence data
ICP-MS
HPLC-CVAFS

ABSTRACT

Concentrations of lead, mercury, cadmium, arsenic, tin, copper and chromium were measured in a study carried out in 2010–2011. A total of 8100 food samples were collected and composite samples for 12 food groups were analysed for metal concentration levels. Metal levels were, in general, below the maximum levels set by the current European legislation. The fish group presented the highest Cd, Hg and As levels, whereas sweeteners and condiments group was the most contaminated food group by Pb, Cr and Sn and the meat group had the highest concentrations of Cu. The results of this study are generally similar to or lower than those observed in other studies conducted in other countries, except in the case of Hg, for which high values were obtained, mainly in swordfish. In addition, this survey confirms a decreasing tendency when compared with other studies carried out in Spain.

1. Introduction

Environmental contamination through heavy metals is recognised as a public health hazard worlwide [1]. The general population is exposed to a large number of relevant contaminants such as metals through food consumption, water and other environmental matrices. Diet (food and water) is the main route of exposure to metals [2]. Some metals are relevant toxic elements such as Pb, Cd, As, Cr (VI) and Hg or minor toxic metals (Sn), whereas others are considered essential or probably essential trace elements with likely potential toxicity at excess intakes such as Cu and Cr (III). Besides, mercury can occur as inorganic mercury, mercuric cations and organic mercury. Methylmercury (meHg) is by far the most common form of organic mercury in the food chain [3]. Regarding arsenic, the organic form is less harmful than the inorganic form of arsenic (iAs) which can cause cancer [4]. Nevertheless, the last EFSA Scientific Opinion on arsenic in food [5] shows that occurrence data on arsenic are usually reported as total arsenic (approximately 98%).

Although the European Commission adopted the Regulation 1881/2006 [6] setting maximum levels for Cd, Hg, Sn, iAs and Pb in foodstuffs, Member States should monitor and report levels of these elements to allow the Commission to assess the need to modify existing measures or to adopt additional ones. In addition, it is of great importance to determine the concentrations of metals in foodstuffs in order to calculate the dietary exposure, required to evaluate the possible risk associated through food consumption.

The dietary exposure of a population to food contaminants can be assessed by different approaches [7]. The World Health Organization (WHO) recommended the so-called total diet studies (TDSs) [8] and nowadays the standardised methodology recommended by the WHO [8] or more recently by EFSA [9] is the most widely used in many countries.

In 2008, the results of a monitoring programme on cadmium, lead and mercury in fish and seafood was carried out by the Department of Public Health of the Valencian government, Spain [10]. The estimated dietary exposure of these pollutants was also reported. However, a representative dataset on food consumption is more appropriate to derive the dietary exposure. Consequently, a new study was carried out in the Region of Valencia in which a representative dataset on food consumption was combined with data on the concentration of the compounds of interest in foods to derive the exposure.Over the last years, some studies have reported metal occurrence data in several countries such as France [11], UK [12] or Chile [13]. In Spain, other studies have also allowed the acquisition of data on the concentrations of trace elements in foodstuffs from Catalonia [14,15] or Canary Islands [16]. In 2008, a study was carried out in Valencia [17] to determine the levels

* Corresponding author.
E-mail address: yusa_vic@gva.es (V. Yusà).

https://doi.org/10.1016/j.toxrep.2018.05.005
Received 10 December 2017; Received in revised form 2 May 2018; Accepted 13 May 2018
Available online 21 May 2018

of mercury, cadmium and lead in fish and seafood marketed in the Region of Valencia using data from monitoring. To complement this study, in 2010–2011, the Public Health Directorate of the region of Valencia started the Valencia Total Diet Study, to estimate the dietary exposure to toxic and essential elements in order to assess the derived health risk. The data in the context of a health risk assessment was reported previously [18]. The present study contains more detail on analytical methods and more complete reporting of the results. The data presented are of great interest as it can be used for regulatory purposes.

The aim of this work was to present metal occurrence data in foodstuffs collected in the region of Valencia for Pb, Cd, As, Hg, Cu, Cr and Sn and to compare these results with those obtained in other countries or in different regions in Spain, and, when available, to compare these results with the maximum levels established by law [6].

2. Material and methods

2.1. Samples

Foodstuffs were selected to be representative of the diet of the population of the Region of Valencia. Two main criteria were considered for selecting the food in the study: (1) the most consumed foods in terms of quantity (> 2 g/person and day) according to the food consumption data of the region of Valencia and (2) foods that are known to contribute the most to exposure to the metals of interest (swordfish or tuna in the case of meHg or offal for Cd [22,30]). A total of 81 different individual foods were selected and aggregated into twelve food groups. To minimise the variability, each food was composed of a hundred samples, collected in different areas (covering rural and urban areas in different geographic locations) and seasons, so the total number of samples purchased was 8100. In order to reduce the number of analysis, a composite sample was formed by 10 individual samples of the same food, so the total number of analysis was 810 for each metal, except for mercury that was only analysed in fish and seafood products (120 analysis) (Table 1).

Two fundamental criteria were considered for designing the sampling plan: the type of establishment and its geographical location. The sampling was carried out in two stages: (1) Selection of a random cluster sample corresponding to different geographical areas or core areas of the Valencian Region; being the sample size assigned to each cluster proportional to the population that it represented, and (2) A new selection using stratified random sampling based on the type of establishment. Four types of establishments were considered: 3 food chains supplying an important part of the Valencian region population (30% each) and local markets (10%). Finally, samples were collected in 11 cities of the Region of Valencia, with over 25.000 inhabitants each, at their respective markets and supply chains (see Fig. S.I.1 in the supplementary information online).

Only edible parts of each food were included in the composites. Kitchen utensils were used for food handling. Food was homogenised with a Thermomix TM-21 food processor and the obtained mixture was divided into 100 g or mL aliquots. These composite samples were stored in high-density polyethylene bags. For maximum stability and homogeneity of samples, fresh samples (high water content) were previously lyophilised with a Telstar LyoAlfa 15 lyophiliser and sent to the laboratory for analysis.

2.2. Reagent and standard solutions

All reagents used in this study were Suprapur-type (Merck, Darmstadt, Germany), or of high analytical grade. Reagents and samples were prepared using analytical reagent grade chemicals and ultrapure water type I (ASTM) generated by purifying distilled water with a Milli-Q Gradient A10 system (Merck Millipore S.A., Merck KGaA, Darmstadt, Germany).

2.3. Analysis

The samples were analysed in two different laboratories: the Public Health Laboratory (Alicante) and the Institute of Agrochemical and Food Technology (Valencia), accredited following the ISO/IEC 17,025 standard [19]. The analytical techniques used fulfilled the criteria set in Regulation (EC) Nº333/2007 [20]. All analyses were performed according to protocols of quality assurance, including duplicate samples, reagent blanks, fortified samples and certified reference materials. Detailed methodologies are described in the following sections:

2.3.1. Analysis of Pb, Cd, total As (tAs), Cu, Cr and Sn

The digestion of lyophilised samples was carried out using a microwave digestion system, Ethos one (Milestone Inc., Shelton, USA), equipped with the Q-20 Quartz Rotor Ultratrace Analysis (20 mL quartz

Table 1
Foodstuffs included in the total diet study, data sampling design.

Food group	Foodstuffs	Nº Total samples	Nº total of composites (or analysis)
Vegetable oils (Vo)	Olive oil and sunflower oil	200	20
Mineral water (Mw)	Mineral water	100	10
Alcoholic beverages (Ab)	Wine and beer	200	20
Non-alcoholic beverages (nAb)	Soda and soft drinks, orange juice, multi-fruits juice	300	30
Meat and meat products (Meat)	Chicken, pork, beef, lamb, rabbit, hamburgers, sausages, cured ham, cooked ham, cured sausages, foie-grass and offal.	1200	120
Cereals, pulses, tuber, nuts and dried fruits (Cereal)	Rice, industrial bakery, cornflakes, cookies, beans, white bread, sliced bread, wholemeal bread, pasta, potatoes, dried fruits.	1100	110
Prepared dishes (Pd)	Pizzas, snacks, frozen prepared dishes and canned meals	400	40
Sweeteners and condiments (Sc)	Chocolate and cacao, sugar, salt, sweets and sauces and mayonnaise	500	50
Vegetables and fruits (Vf)	Spinaches and chards; lettuces; green beans; onions; garlic; peppers; aubergine, zucchini and cucumber; carrots and pumpkin; tomatoes; olives and pickles; cauliflower, cabbage and broccoli; artichokes, celery and leek; mushrooms; coffee and soluble coffee; oranges; strawberries; apples and pears; sherry and plum; melon and watermelon; banana; peach and apricot; grapes.	2200	220
Eggs (Egg)	Chicken eggs	100	10
Milk and dairy products (Milk)	Milk, cheese, yogurt, custards and smoothie, butter and soybean products	600	60
Fish and seafood (Fish)	Canned fish, tuna, squid and cuttlefish, sea bream and sea bass, swordfish, shellfish, mussels, whitefish, salmon and trout, sardine and anchovy, salting fish and smoked fish.	1200	120

Note: Number of samples/food item = 100.
Number of samples/composite = 10.